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Investigation of the Interaction of CO_2 with Poly(L-lactide), Poly(DL-lactide) and Poly(ε-caprolactone) using FTIR Spectroscopy

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ABSTRACT: Fourier transform infrared (FTIR) spectroscopy was used to reveal intermolecular interactions between carbon dioxide (CO_2) and the carbonyl groups of poly(L-lactide) (PLLA), poly(D,L-lactide) (PDLLA), and poly(ε-caprolactone) (PCL). After exposing polymer films to high pressure CO_2, the wave number of the absorption maxima of the polymer carbonyl groups shifted to higher values. Also, due to the interaction between CO_2 and the carbonyl groups of the polymers, a new broad peak in the bending mode region of CO_2 appeared. To distinguish between polymer-associated and nonassociated CO_2, and to quantify these contributions, the bending mode peaks were deconvoluted. From these contributions, it was found that in the case of PCL more CO_2 is interacting with the polymer carbonyl groups than in the case of PDLLA and PLLA. Under our experimental conditions, 40°C and pressures up to 8 MPa, a significant depression of the PCL melting temperature was observed. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 109: 3376–3381, 2008

Key words: FTIR spectroscopy; biodegradable polymers; carbon dioxide; processing aid; melting temperature

INTRODUCTION

Because of their favorable mechanical properties, biocompatibility, and degradability, aliphatic polyesters such as poly(L-lactide) (PLLA), poly(D,L-lactide) (PDLLA), and poly(ε-caprolactone) (PCL) are frequently used for biomedical applications.[1–3] These polymers can be applied in the form of sutures, drug delivery systems, and tissue engineering scaffolds. Biomedical implants from these polymers are usually produced by conventional melt processes such as extrusion and injection molding.[4–9]

Especially for polylactides, thermal instability is a major concern with regard to their processing. Amorphous PDLLA has a glass transition temperature of ~ 55°C, semicrystalline PLLA melts at ~ 180°C. While PDLLA can be extruded and molded at temperatures close to 150°C, thermal processing of PLLA needs to take place at temperatures exceeding 200°C. Thermal degradation of polylactides in the molten state has been widely studied.[4–12] This mainly occurs by random main-chain scissions. Apart from the effect of temperature, degradation is also influenced by the presence of residual monomer, catalyst, air, and moisture. However, the role of temperature is decisive, as the rate of degradation decreases with decreasing temperature.[11] As a result of degradation reactions, polymers can exhibit significant losses of their molecular weight. Taubner and Shishoo[6] have reported a 20% reduction in the molecular weight of the polymer after extrusion at 210°C. This reduction in molecular weight results in deterioration of stress and strain at break of the final product.

PCL is a semicrystalline polymer with a low melting temperature of ~ 60–65°C. Its main uses are in the preparation of drug delivery devices and tissue engineering scaffolds.[2,3,13] In general, the polymer does not undergo excessive degradation during thermal processing.[14] However, when compounding thermally sensitive drugs into polymer matrices, as required in the preparation of drug releasing systems, a low processing temperature is essential.

A plasticizer allows the processing of these polymers at low temperatures. Recently, supercritical carbon dioxide (CO_2) has been established as a solvent and plasticizer in the synthesis and processing of various polymers.[15] Advantages of the use of CO_2 are its inert (nontoxic) nature and that it can be easily removed by simple depressurization. At supercritical conditions (temperatures in excess of 31°C and pressures above 7.38 MPa), its liquid-like

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densities and gas-like diffusivities allow CO_2 to be used as a conventional solvent and plasticizer. Dissolution of CO_2 in a polymer depresses its glass transition temperature (T_g) and in the case of semicrystalline polymers, its melting temperature (T_m) and the polymer can be processed at a lower temperature. Howdle and coworkers[16] successfully prepared poly (D,L-lactide) micro-particles using supercritical CO_2 at a temperature of 35°C, which is well below the T_g of the polymer (T_g is $\sim$ 55°C). The morphology, cell size, and porosity of the final products could readily be controlled by variation of the temperature and CO_2 pressure applied.

The shear viscosity of a polymer decreases with increasing amounts of dissolved CO_2. The amount of CO_2 that can be dissolved in a polymer depends on the type of polymer, the applied temperature, and pressure. Polymers containing ester bonds generally show good solubility of CO_2 due to Lewis-acid–base interactions between CO_2 and the carbonyl groups.[17] Several authors have investigated this specific intermolecular interaction for different polymers by Fourier Transform Infrared (FTIR) spectroscopy.[18–24] In the presence of dissolved CO_2 (either at sub- or supercritical conditions), shifts in the wave number of the carbonyl stretching vibrations of cellulose acetate (CA), poly(methyl methacrylate) (PMMA), poly (carbonate) (PC), and ethoxylated and propoxylated polyester resins have been reported. Furthermore, the bending mode of CO_2 (ν_2, at $\sim$ 660 cm^{-1}) is also indicative of these interactions as shown by Kazarian et al.[21] and Nalawade et al.[24]

In this study, the interaction between PLLA, PDLLA and PCL and CO_2 at pressures up to 8 MPa (80 bar) was investigated using FTIR spectroscopy. Moreover, the study was used to determine the depression in the melting temperature of PCL polymers as a function of CO_2 pressure.

EXPERIMENTAL

Materials

PLLA and PDLLA were supplied by Purac Biochem, The Netherlands. The viscosity average molecular weights (M_w) were respectively, 225,000 and 325,000, as determined from intrinsic viscosity measurements in chloroform at 25°C.[25] Poly(ε-caprolactone) (PCL) with a weight average molecular weight (M_w) of 3000 (PCL3) and 50,000 (PCL50) were supplied by Solvay, UK. Table I shows the glass transition temperatures (T_g) and the melting temperatures (T_m) of the polymers. For poly(lactide)s, the temperatures were obtained by a differential scanning calorimetry apparatus (Pyris 1, Perkin–Elmer, USA) at a heating rate of 10°C/min. In case of PCL, these temperatures were provided by the supplier. Analytical grade chloroform ($CHCl_3$) was purchased from Aldrich, The Netherlands. High purity CO_2, 99.9%, was used in our experiments.

TABLE I
Thermal Properties of the Polymers Used

Polymer	T_g (°C)	T_m (°C)
PDLLA	47	–
PLLA	59	181
PCL3	−60	57
PCL50	−61	60

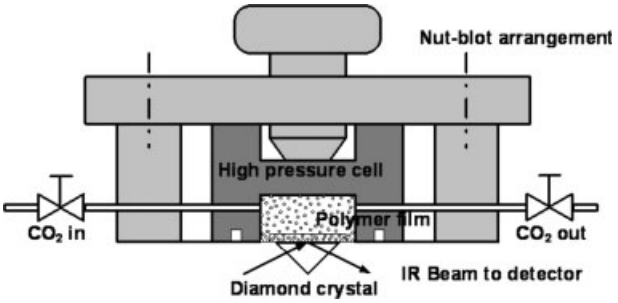

Figure 1 Schematic drawing of a high pressure, ATR FTIR setup to measure IR absorption at high CO_2 pressures.

High pressure IR spectroscopy

To study the interaction of CO_2, with the different polymers, a Fourier Transform Infra Red spectroscopy (FTIR) apparatus (Spectrum 2000, Perkin–Elmer, UK) was modified to allow measurements at high CO_2 pressures. A Golden Gate™ single attenuated total reflection (ATR) reflection system, containing a diamond crystal, was employed together with a custom-built high pressure cell.

The setup also includes a CO_2 cylinder, a high pressure syringe pump (Isco, USA), and high pressure valves. To be able to operate at supercritical CO_2 conditions, electrical heating elements were used to reach a temperature of 40°C at an accuracy of 0.5°C. A schematic drawing is shown in Figure 1. IR spectra ranging from 500 to 4000 cm^{-1} were obtained at temperatures of 40°C and CO_2 pressures up to 8 MPa (80 bar). For reasons of safety, higher operating temperatures at high pressures were not feasible in our setup.

Polymer films were directly prepared on the ATR diamond crystal. Thin PCL films were formed by spreading a small amount of molten polymer on the diamond crystal, heated to 65°C by a heating plate, and subsequent cooling. Small amounts of PLLA and PDLLA solutions in chloroform (concentration

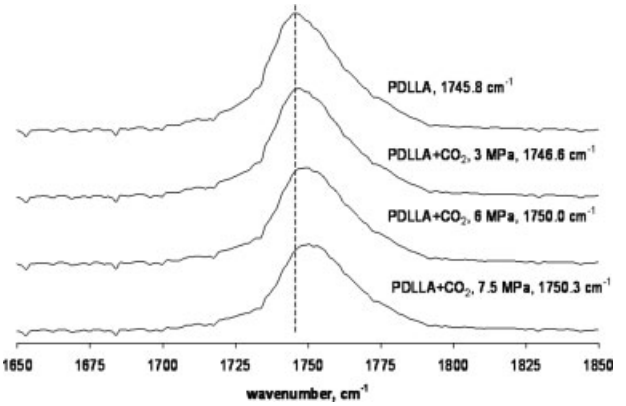

Figure 2 FTIR spectra of PDLLA at different CO_2 pressures. The interaction with CO_2 results in a shift in the absorption maximum of the stretching vibrations of the carbonyl groups.

of ~ 3 g/100 mL) were placed directly onto the surface of the diamond crystal. After evaporation for few hours, thin films were obtained. After heating the polymer film and pressure cell to 40°C a reference spectrum was recorded in the absence of pressurized CO_2. To carry out measurements at high CO_2 pressures, the cell was first flushed extensively to remove air. The outlet valve was then closed, and after reaching the desired pressure the inlet valve was closed as well. Before recording the absorption spectra, isobaric and isothermal conditions were maintained for at least 30 min. FTIR measurements at CO_2 pressures increasing from 0 to 8 MPa were conducted on a single polymer film. CO_2 absorption spectra, in the absence of polymer were recorded as well. The FTIR spectra are the average of 60 scans obtained at a high resolution of 2 cm^{-1}. To deconvolute overlapping absorption bands a software package (Peak-fit, UK) was used.

RESULTS AND DISCUSSION

Interaction of CO_2 with polymer carbonyl groups

FTIR spectra showing the stretching vibrations of the carbonyl groups (C=O) of the PDLLA polymer, that was exposed to different CO_2 pressures, are shown in Figure 2. The absorption maximum of the PDLLA carbonyl group appears at a wave number of 1746 cm^{-1}. With increasing CO_2 pressure, this wave number shifts to a higher value. These shifts result from the weak Lewis acid–base interaction between CO_2 and the carbonyl group of the polymer: the frequency of vibration of the carbonyl group is reduced in the presence of CO_2, and consequently the wavenumber shifts to a higher value. In previous reports on the interaction of CO_2 with PMMA, comparable changes in carbonyl absorption maxima were found.[20]

Similar effects were observed for PLLA and PCL of different molecular weights upon increasing the CO_2 pressure. Table II gives wavenumbers (corresponding to the absorption maxima) of the carbonyl groups of all polymers in the absence and presence of CO_2. For all polymers, the shift in wavenumber reaches a limit at higher pressures as a result of increased mobility of CO_2 at higher pressures. At these pressures, the increased number of CO_2–CO_2 interactions compete with CO_2–carbonyl interactions.[21] By comparing the results of PLLA with PDLLA, it can be seen that under our experimental conditions the crystallinity of the polymer apparently does not influence the shift in wavenumber. In both cases, Table II shows that the largest shift in wavenumber occurs at a CO_2 pressure of 6 MPa. For PCL3 the largest shift in wavenumber occurs at 3 MPa, while for PCL 50 this is at 6 MPa. This can be the result of differences in solubility of CO_2 in the polymer: it is to be expected that CO_2 solubility decreases with polymer molecular weight. Furthermore, its melting point is slightly lower.

In these pressure ranges, the amount of CO_2 that can be dissolved in a polymer increases linearly with increasing pressure.[26] Although the relationship between CO_2 pressure and absorption maximum (or shift in absorption maximum) in our experiments was not linear, the integral area of the carbonyl peaks decreased linearly with increasing pressure. As a result of the increasing pressure, the CO_2 molar fraction in the film contacting the diamond crystal surface increases.

TABLE II
The Wave Numbers of the Carbonyl Groups of the Polymers in the Absence and Presence of High Pressure CO_2

	Wave number, cm^{-1}					
Polymer	0 MPa	1.5 MPa	3 MPa	6 MPa	7.5 MPa	8 MPa
PDLLA	1745.8	–	1746.6	1750.0	–	1750.3
PLLA	1747.6	–	1750.4	1755.6	–	1755.3
PCL3	1721.0	1721.0	1728.9	1729.1	1729.4	–
PCL50	1721.4	1721.3	1721.5	1729.1	1729.5	–

–, experiment not performed.

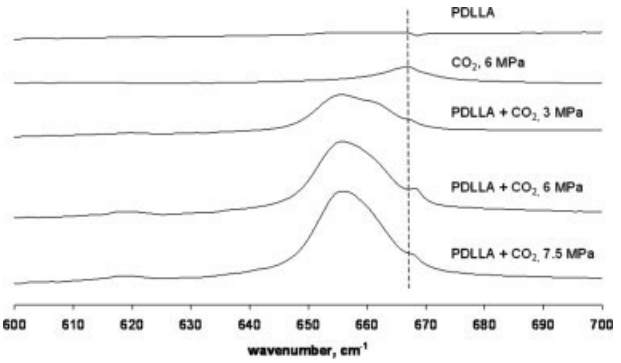

Figure 3 FTIR spectra showing the bending mode vibration (ν_2) of CO_2 and of CO_2 in contact with PDLLA at different pressures.

When considering the IR absorption spectra of CO_2 in these experiments, shifts in absorption maxima can be observed as well. These changes are especially evident in the bending mode (ν_2) region of CO_2. Figure 3 shows the absorption spectra of the bending mode region of CO_2 dissolved at different pressures in PDLLA films.

In the absence of PDLLA, a distinctive CO_2 peak is observed at 667 cm^{-1}. At different pressures, in the presence of PDLLA, a broad peak with a maximum close to 655 cm^{-1} can be observed. In the presence of CO_2 a small shoulder appeared close to 667 cm^{-1} on the broad peaks which represents free (nonassociated) CO_2. Kazarian et al.[21] have reported such a broad peak in the bending mode region of CO_2 for a PMMA film subjected to different CO_2 pressures. Similar observations were made for PLLA, PCL50, and PCL3 in our studies. Figure 4 shows the absorption spectra of the bending mode region of CO_2 dissolved at different pressures in PCL50 films. Besides the peak in the bending mode region of CO_2, a small unknown absorption peak at 618 cm^{-1} in the presence of CO_2 was observed.

It can clearly be seen from Figures 3 and 4 that the area beneath the peak corresponding to the CO_2 bending mode (ranging from 640 to 670 cm^{-1}) increases with increasing CO_2 pressure. By deconvolution of the peak, the contribution of associated and nonassociated CO_2 to the IR absorbance can be quantified. Kazarian et al. deconvoluted the peak into different peaks corresponding to associated CO_2 (close to 655 cm^{-1}) and nonassociated CO_2 (close to 665 cm^{-1}).[21] As previously mentioned, this association arises from the interaction of CO_2 with the carbonyl groups of the polymers. Table III gives the magnitudes of integral areas of the deconvoluted ν_2 bending mode absorbances of the different polymers pressurized at 6 MPa CO_2.

The relative amount of CO_2 interacting with the carbonyl groups of the polymer can be correlated to the amount of CO_2 dissolved. Therefore, from the table it follows that the CO_2 solubility in PCL is the highest, and that the CO_2 solubility in PDLLA is higher than in PLLA. Solubility data of CO_2 in PCL and PLLA at more elevated temperatures and at different pressure ranges are available in the literature.[27,28] By extrapolation of this data, we can predict that the solubility of CO_2 at 40°C and 6 MPa in PLLA is 7 wt %, and in PCL 11 wt %. For PDLLA, no CO_2 solubility data are available. However, for a given polymer varying in crystallinity, the solubility of CO_2 increases with decreasing crystallinity.[29] Therefore, it can be expected that the solubility of CO_2 in amorphous PDLLA is higher than in the semicrystalline PLLA.

Depression of polymer melting temperatures by CO_2

The interaction of CO_2 with the polymer carbonyl groups leads to absorption of CO_2, and as a result of this the glass transition temperature (T_g) and/or the melting temperature (T_m) is/are depressed. Under the studied conditions, in case of the semi crystalline polymers a depression in the melting temperature was expected only for PCL due to its low melting temperature compared to PLLA. The depression can be determined by comparing FTIR absorption spectra of a polymer in the presence of CO_2 with a spectrum of the molten polymer in the absence of CO_2.

FTIR absorption spectra of PCL50 films were obtained in the absence of CO_2 at temperatures of 40 and 80°C, i.e., at a temperature below and above the polymer melting temperature ($\sim$ 60°C). Clear differences could be observed in the region of 900 to 1400 cm^{-1}, as Figure 5 shows. In this region, all peaks except one at $\sim$ 1155 cm^{-1} are strongly reduced or disappear completely upon melting. At 40°C and high CO_2 pressures, the IR spectrum of a PCL50 film

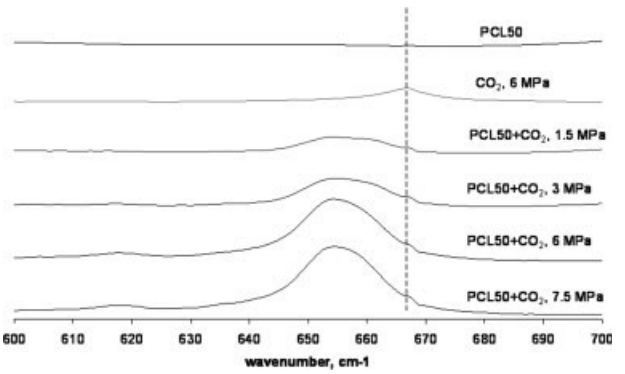

Figure 4 FTIR spectra showing the bending mode vibration (ν_2) of CO_2 and of CO_2 in contact with PCL50 at different pressures.

TABLE III
The Magnitudes of the Integral Areas (Arbitrary Units) of the Deconvoluted CO_2 ν_2 Bending Mode Absorbances of the Different Polymers Pressurized at 6 MPa CO_2

Polymer	Associated CO_2 Peak area[a] ($\sim$ 655 cm^{-1})	Nonassociated CO_2 Peak area[a] ($\sim$ 667 cm^{-1})	% CO_2 Associated
PDLLA	6.3	0.40	94
PLLA	4.3	0.64	87
PCL3	7.7	0.04	99
PCL50	7.3	0.14	98

Contributions of different bending modes of associated CO_2 and of nonassociated CO_2 are distinguished.

[a] The area corresponds to the de-convoluted peaks with maximum absorption at the given wavenumbers. The peaks were obtained by deconvoluting the broad peak obtained in the bending mode region of CO_2 (ranging from 640 to 670 cm^{-1}).

resembles the spectrum of the film at 80°C in the absence of CO_2. This implies that at the former conditions, the polymer is in the molten state. Figure 5 also shows that upon increasing the pressure at 40°C, this transition occurs at a CO_2 pressure above 3 MPa. Similar changes were seen in the IR spectra of the lower molecular weight PCL3 above 1.5 MPa. The lower transition pressure for PCL3 can be related to its slightly lower melting temperature and lower molecular weight. From our experiments with PCL at 40°C, it follows that a reduction in the melting temperature of 20°C can be achieved by application of high pressure CO_2.

To quantify the melting of PCL as a function of CO_2 pressure, the magnitude of the integral area of the peak (area under the peak) ranging from 1120 to 1210 cm^{-1} can be used. These values are presented in Figure 6. In the absence of CO_2 at 80°C, the magnitude of the integral area (arbitrary units) of the peak ranging from 1120 to 1210 cm^{-1} for PCL50 is 13. This value is indicative of the molten state. At 40°C, in the solid semicrystalline state, the value for PCL50 is 22. By plotting these values of the IR absorption spectra of PCL 50 films subjected to different CO_2 pressures at 40°C, we can estimate that PCL50 melts at a higher pressure of $\sim$ 5 MPa.

Like PCL, our FTIR investigations on PDLLA and PLLA at 40°C did not reveal changes in the IR absorption spectra upon pressurizing with CO_2. In our experimental setup, in which we could not simultaneously apply high temperatures and pressures, it was not possible for us to investigate an effect of high pressure CO_2 on reducing the melting temperature of semicrystalline PLLA. At this temperature, a CO_2 pressure significantly higher than 8 MPa will be required.

CONCLUSIONS

FTIR spectroscopy is a useful tool to investigate the interaction of CO_2 with polymer carbonyl groups. In a modified setup, where temperatures and CO_2 pressures can be varied, these investigations can also be carried out using supercritical CO_2. In this way,

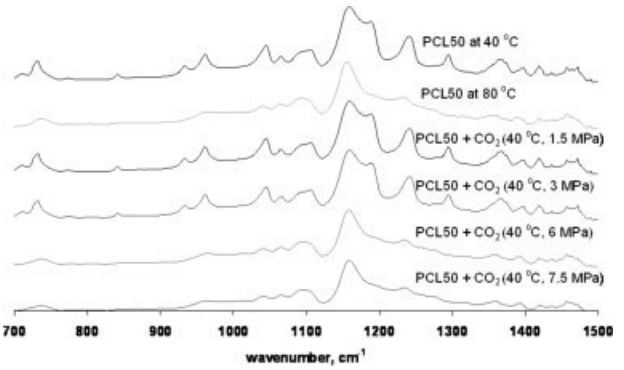

Figure 5 FTIR absorption spectra in the region of 900–1400 cm^{-1} of PCL50 at 40 and 80°C in the absence of CO_2, and at 40°C under different CO_2 pressures.

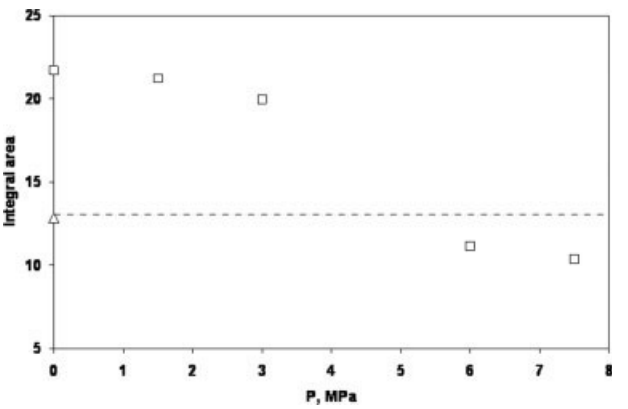

Figure 6 Integral area (arbitrary units) of the IR absorption peak (1120–1210 cm^{-1}) of PCL50 films subjected to different CO_2 pressures at 40°C (□) and integral peak area of PCL50 film at 80°C (△).

polymers suited for CO_2 processing can be selected using minimal amounts of polymer.

Upon dissolution of CO_2 in PDLLA, PLLA, and PCL, changes in the absorption spectra in the regions corresponding to the stretching vibrations of the polymer carbonyl groups and of the CO_2 bending mode vibrations can be observed. In the case of PCL, clear melting temperature reductions upon pressurization with CO_2 can be visualized directly. This study suggests that (supercritical) CO_2 may be advantageously used as a processing aid for PCL. The same might hold for PDLLA and PLLA which melts at a high temperature, but additional experimental work at higher temperatures and higher CO_2 pressures will be required to demonstrate this.

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